Chapter 5
Mercury in the Open-Lake Water Column

Open-lake water column samples were collected during six cruises of the *R/V Lake Guardian* conducted from April 1, 1994 to October 22, 1995. Samples were collected at 17 sampling locations, including 15 stations in Lake Michigan, 1 location in Green Bay and 1 location in Lake Huron (see Figure 2-4). Samples were collected at depths ranging from 1 m to 150 m. Samples were collected as described in Section 2.4.3 and analyzed for total and particulate mercury by cold-vapor atomic fluorescence spectrometry (see Section 2.5.3). In addition, dissolved mercury results were calculated by subtracting the particulate mercury result from the total mercury result, when results from both fractions were reported.

5.1 Results

A total of 121 samples were analyzed for particulate mercury, and a total of 125 samples were analyzed for total mercury (Table 5-1). Particulate mercury results ranged from 0.027 ng/L to 0.30 ng/L, with approximately 8% of the samples below the associated daily detection limit. Total mercury results ranged from 0.037 ng/L to 0.78 ng/L, with approximately 4% of the samples below the associated daily detection limit. Combining data from all depths and all cruises, the lake-wide mean mercury concentrations measured in this study were 0.33 ng/L for total mercury and 0.11 ng/L for particulate mercury.

Table 5-1. Numbers of Open-Lake Samples Analyzed for Mercury

Sampling Station	Sampling Dates	Particulate Samples	Total Mercury Samples	Total Number of Samples
GB24M	08/08/94 to 09/20/95	7	7	14
LH54M	08/03/94 to 09/16/95	10	10	20
05	08/24/94 to 10/10/95	8	8	16
140	06/18/94 to 09/23/95	8	8	16
180	04/07/95 to 04/07/95	1	1	2
18M	06/22/94 to 10/09/95	12[a]	12	24
23M	06/23/94 to 10/03/95	12	12	24
240	06/21/94 to 10/02/95	7	9	16
27M	06/20/94 to 09/27/95	10	10	20
280	04/01/95 to 04/01/95	1	1	2
340	08/21/94 to 10/06/95	7	7	14
380	03/26/95 to 03/26/95	1	1	2
40M	10/18/94 to 09/25/95	7	8	15
41	06/18/94 to 10/22/94	4	5	9
47M	06/17/94 to 09/19/95	12	12	24
19M	08/19/94 to 10/05/95	8	8	16
72M	08/04/94 to 09/17/95	6	6	12
	Total	121	125	246

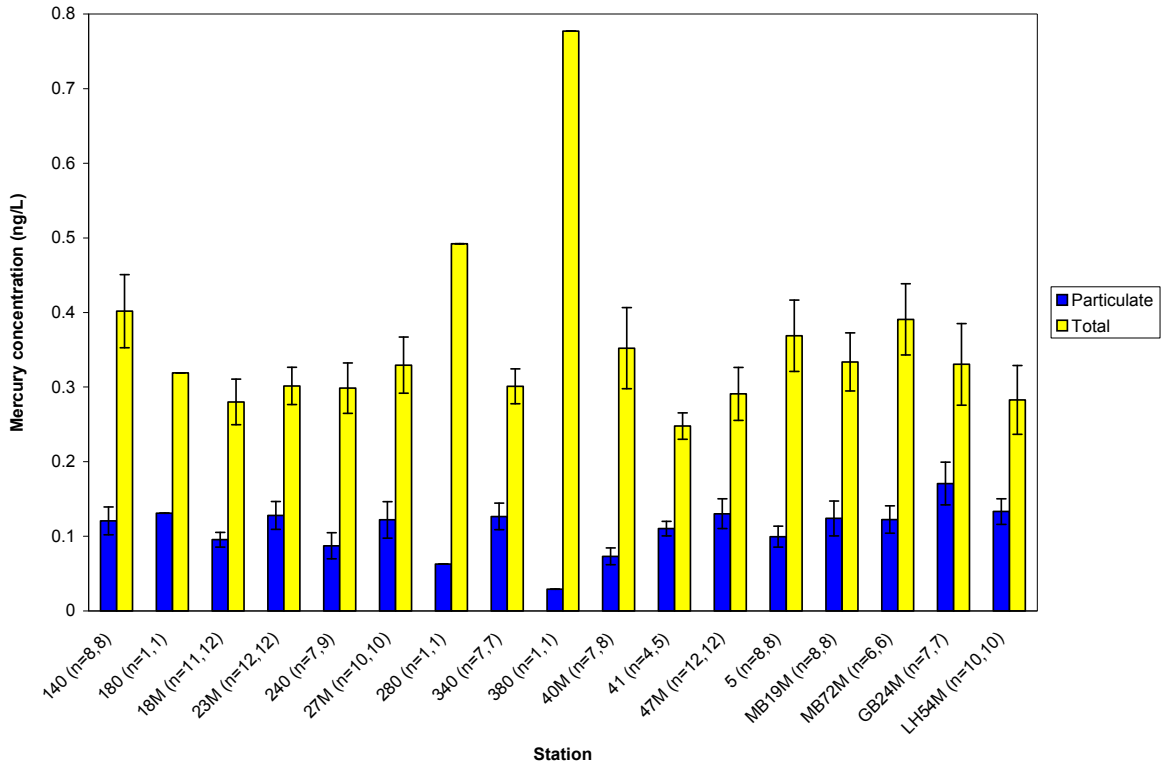
[a] One sample was invalid.
GB = Green Bay station
LH = Lake Huron station

5.1.1 Geographical Variation

From 1 to 12 samples were collected at each of 17 different stations in Lake Michigan, Green Bay, and Lake Huron. The mean concentrations are shown in Figure 5-1, and descriptive statistics of the particulate and total mercury concentrations reported at each station are presented in Table 5-2. Mean particulate mercury concentrations ranged from 0.029 ng/L at Station 380 to 0.17 ng/L at Station GB24M in Green Bay. The maximum mean particulate mercury concentration in Lake Michigan was 0.13 ng/L, and occurred at five different stations. Mean total mercury concentrations ranged from 0.25 ng/L at Station 41 to 0.78 ng/L at Station 380. While the mean particulate and total mercury concentrations collected at Station 380 were extremely low and high, respectively, compared to the other stations, these means only represent a single sample result at this station. Therefore, it is unlikely that these means are representative of the mercury concentrations at that station.

The highest mean particulate mercury value was in Green Bay (GB24M). This finding is not unexpected, due to the large inputs of mercury, particularly in the particulate phase, from the Fox River (see Chapter 4). While particulate mercury concentrations were slightly higher in Green Bay than other sampling sites, there were no significant differences among site in particulate mercury concentrations, based on a one-way Analysis of Variance (ANOVA) model using log-transformed results (p=0.1685). Mean total mercury concentrations were relatively consistent throughout Lake Michigan. No statistical differences were observed among sampling sites, based on a one-way ANOVA model using log-transformed results (p=0.2309).

Figure 5-1. Mercury Concentrations Measured in Open-lake Water Column Samples



Stations are from Lake Michigan except for GB24M (Green Bay) and LH54M (Lake Huron). Bars show the mean mercury concentration of samples collected at each station for the duration of the study. Error bars are standard error.

Table 5-2. Mean Particulate and Total Mercury Concentrations Measured in Open Lakes

Fraction	Sampling Station	N	Mean (ng/L)	Median (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	Below DL (%)
Particulate	140	8	0.12	0.12	0.049 to 0.19	0.053	44	13
	180	1	0.13	0.13	NA	NA	NA	0.0
	18M	11	0.095	0.094	0.030 to 0.15	0.033	35	0.0
	23M	12	0.13	0.11	0.031 to 0.24	0.065	51	0.0
	240	7	0.087	0.063	0.038 to 0.16	0.046	53	14
	27M	10	0.12	0.12	0.030 to 0.30	0.077	63	10
	280	1	0.063	0.063	NA	NA	NA	0.0
	340	7	0.13	0.13	0.05 to 0.19	0.047	37	0.0
	380	1	0.029	0.029	NA	NA	NA	0.0
	40M	7	0.073	0.073	0.038 to 0.11	0.029	40	0.0
	41	4	0.11	0.10	0.097 to 0.14	0.020	18	0.0
	47M	12	0.13	0.13	0.035 to 0.28	0.070	53	17
	5	8	0.10	0.10	0.032 to 0.15	0.040	40	25
	GB24M	7	0.17	0.19	0.076 to 0.30	0.076	45	14
	LH54M	10	0.13	0.12	0.079 to 0.27	0.054	41	20
	19M	8	0.12	0.13	0.027 to 0.20	0.066	53	0.0
	72M	6	0.12	0.13	0.057 to 0.17	0.045	36	0.0
Total	140	8	0.40	0.42	0.21 to 0.61	0.14	35	0.0
	180	1	0.32	0.32	NA	NA	NA	0.0
	18M	12	0.28	0.27	0.14 to 0.46	0.11	38	8.3
	23M	12	0.30	0.30	0.21 to 0.48	0.086	29	8.3
	240	9	0.30	0.27	0.19 to 0.48	0.10	34	0.0
	27M	10	0.33	0.28	0.22 to 0.57	0.12	36	0.0
	280	1	0.49	0.49	NA	NA	NA	0.0
	340	7	0.30	0.30	0.22 to 0.39	0.062	21	0.0
	380	1	0.78	0.78	NA	NA	NA	0.0
	40M	8	0.35	0.30	0.19 to 0.57	0.15	44	13
	41	5	0.25	0.25	0.19 to 0.30	0.040	16	0.0
	47M	12	0.29	0.28	0.075 to 0.48	0.12	42	8.3
	5	8	0.37	0.33	0.19 to 0.55	0.14	37	0.0
	GB24M	7	0.33	0.29	0.16 to 0.56	0.14	44	0.0
	LH54M	10	0.28	0.34	0.037 to 0.49	0.15	52	10
	19M	8	0.33	0.30	0.20 to 0.54	0.11	33	0.0
	72M	6	0.39	0.34	0.30 to 0.59	0.12	30	0.0

NA = Not applicable
GB = Green Bay station
LH = Lake Huron station

Statistical comparisons also were performed after combining the 15 stations in Lake Michigan into two different basins. For these comparisons, the data from the LMMB Study were divided at approximately 44° north latitude. The dividing line at 44° N is not intended as a formal differentiation between hydrographic basins in the lake, and other means of differentiating the results from north to south could be considered. The latitude limit was instead chosen to remain consistent with analyses performed on PCB and atrazine data. The results from the stations in Green Bay and Lake Huron were excluded from these comparisons. Based on the 44° N dividing line, six of the 15 Lake Michigan stations were categorized as being in the northern basin (40M, 41, 47M, 72M, 140 and 180).

The results of the basin comparisons were similar to those of the comparisons of individual stations. For both particulate and total mercury, there were no significant differences in mercury concentration between basins (particulate: $p = 0.1046$; total: $p = 0.2523$) or between stations nested within basin (particulate: $p = 0.3869$; total: $p = 0.0805$).

The lack of spatial differences is consistent with previous assessments that suggest that the primary source of mercury is atmospheric rather than riverine (Mason and Sullivan, 1997). The effect of the variability in mercury concentration among the tributaries, as discussed in Chapter 4, is only seen in the slightly greater particulate mercury concentration in Green Bay at station GB24M. However, the total mercury concentration at this station did not exhibit any effect of the Fox River, as the mean concentration of 0.30 ng/L was below the overall mean total mercury concentration. Therefore, it is likely that most of the mercury from the Fox River is removed to the sediment rather than staying in the water column (Sullivan and Mason, 1998).

5.1.2 Seasonal Variation

Samples were collected during six cruises: June 1994, August 1994, October/November 1994, March/April 1995, August 1995 and September/October 1995. During each cruise, up to 2 samples were collected at each station. Descriptive statistics for particulate and total mercury for each cruise are presented in Table 5-3.

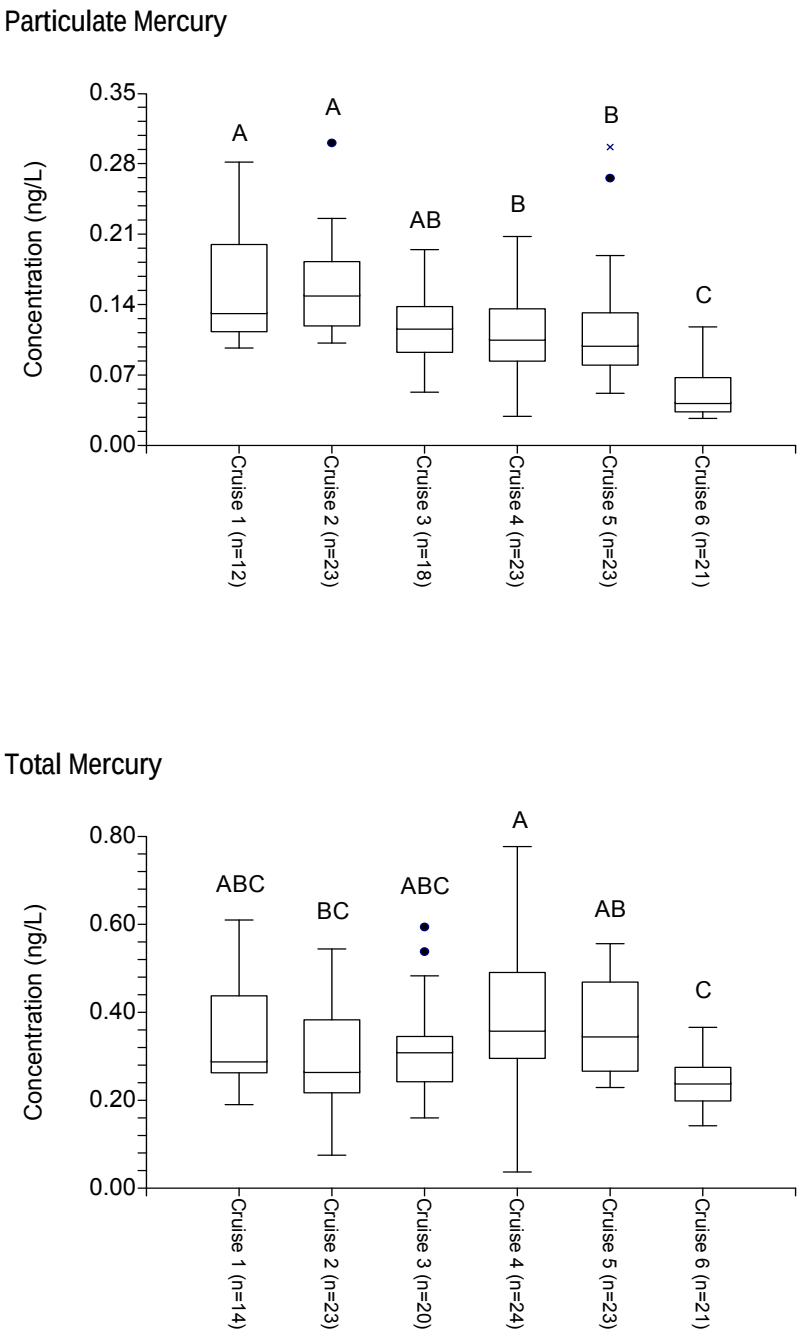
Table 5-3. Mean Particulate and Total Mercury Concentrations by Cruise

Fraction	Sampling Cruise	N	Mean (ng/L)	Median (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)	Below DL (%)
Particulate	June 1994	12	0.16	0.13	0.097 to 0.28	0.060	37	0.0
	August 1994	23	0.16	0.15	0.10 to 0.30	0.047	30	43
	Oct./Nov. 1994	18	0.12	0.12	0.053 to 0.20	0.039	32	0.0
	March/April 1995	23	0.11	0.11	0.029 to 0.21	0.040	37	0.0
	August 1995	23	0.12	0.10	0.052 to 0.30	0.062	53	0.0
	Sept./Oct. 1995	21	0.052	0.043	0.027 to 0.12	0.024	46	0.0
Total	June 1994	14	0.34	0.29	0.19 to 0.61	0.12	35	0.0
	August 1994	23	0.29	0.27	0.075 to 0.54	0.12	41	13
	Oct./Nov. 1994	20	0.33	0.31	0.16 to 0.59	0.12	36	0.0
	March/April 1995	24	0.38	0.36	0.037 to 0.78	0.16	41	8.3
	August 1995	23	0.36	0.35	0.23 to 0.56	0.10	29	0.0
	Sept./Oct. 1995	21	0.24	0.24	0.14 to 0.37	0.062	26	0.0

Mean particulate mercury concentrations generally decreased over the course of the study, ranging from 0.16 ng/L in the June and August 1994 cruises to 0.052 ng/L in the autumn 1995 cruise. Based on a one-way ANOVA model, the difference between cruises was significant ($p<0.0001$). Subsequent Tukey pairwise comparisons showed that the means for the first two cruises were significantly greater than the means for the last three cruises, and that the mean of the last cruise was significantly lower than the means for all other cruises (Figure 5-2A). Unlike particulate mercury, mean total mercury concentrations did not appear to follow a trend. The maximum mean total mercury concentration occurred in March/April 1995, rather than in summer 1994. However, similar to particulate mercury, the minimum concentration occurred in September/October 1995. A one-way ANOVA model comparing mean total mercury concentrations between cruises was statistically significant ($p = 0.0015$). Tukey pairwise comparisons showed that the means of the March/April and August 1995 cruises were significantly greater than the mean for the September/October 1995 cruise and that the mean of the March/April cruise was significantly greater than the mean of the August 1994 cruise (Figure 5-2B).

Because the timing of the cruises differed between the two years of collection, it is difficult to interpret the concentration differences between cruises as seasonal or annual differences. Cruises 2 and 5 occurred during August, however, and differences could be interpreted as due to differences between 1994 and 1995. Based on profiles of temperature and pH, Sullivan and Mason (1998) concluded that productivity in the lake was lower in the summer of 1994 compared to the summer of 1995. They hypothesize that the increase in pH from August 1995 to September/October 1995 is evidence of the pH-induced precipitation of calcite, a mineral form of calcium carbonate, and they conclude that the seasonal dynamics of the lake differed between the two years of the LMMB Study. These differences in dynamics may have an effect on the concentrations and partitioning of mercury in the lake.

Figure 5-2. Particulate and Total Mercury Concentrations Measured in Open Lakes, by Cruise



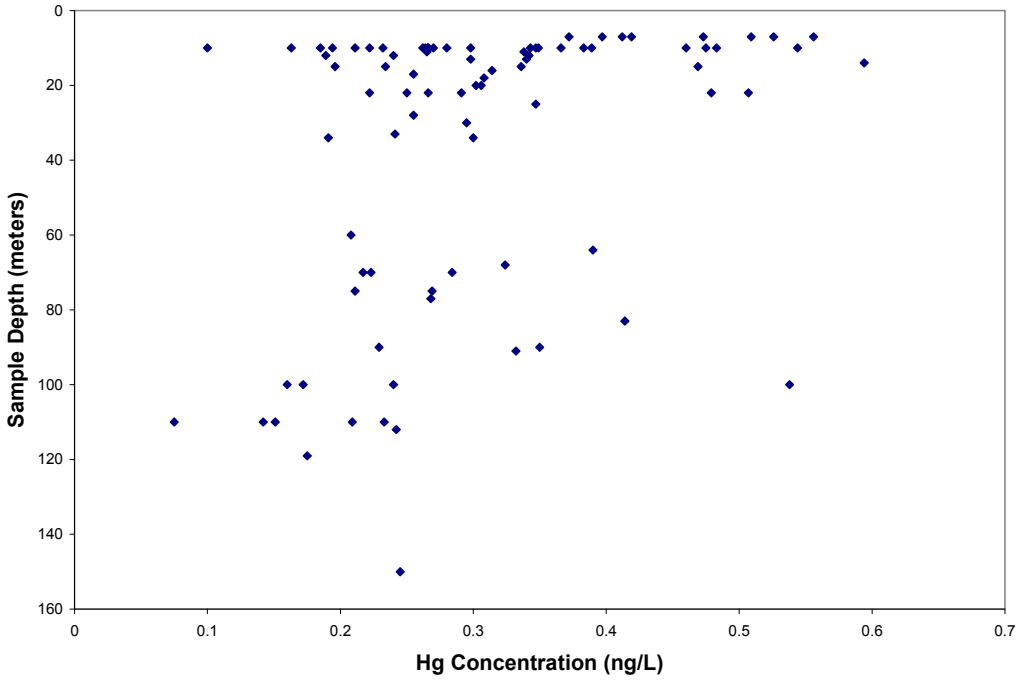
Cruise 1 = June 1994, Cruise 2 = August 1994, Cruise 3 = September/October 1994, Cruise 4 = March/April 1995, Cruise 5 = August 1995, and Cruise 6 = September/October 1995

Boxes represent the 25th (box bottom), 50th (center line), and 75th (box top) percentile results. Bars represent the results nearest 1.5 times the inter-quartile range (IQR=75th-25th percentile) away from the nearest edge of the box. Circles represent results beyond 1.5*IQR from the box. Xs represent results beyond 3*IQR from the box. Letters above the boxes represent results of analysis of variance and multiple comparisons test. Boxes with the same letter were not statistically different (at alpha = 0.05).

5.1.3 Vertical Variation

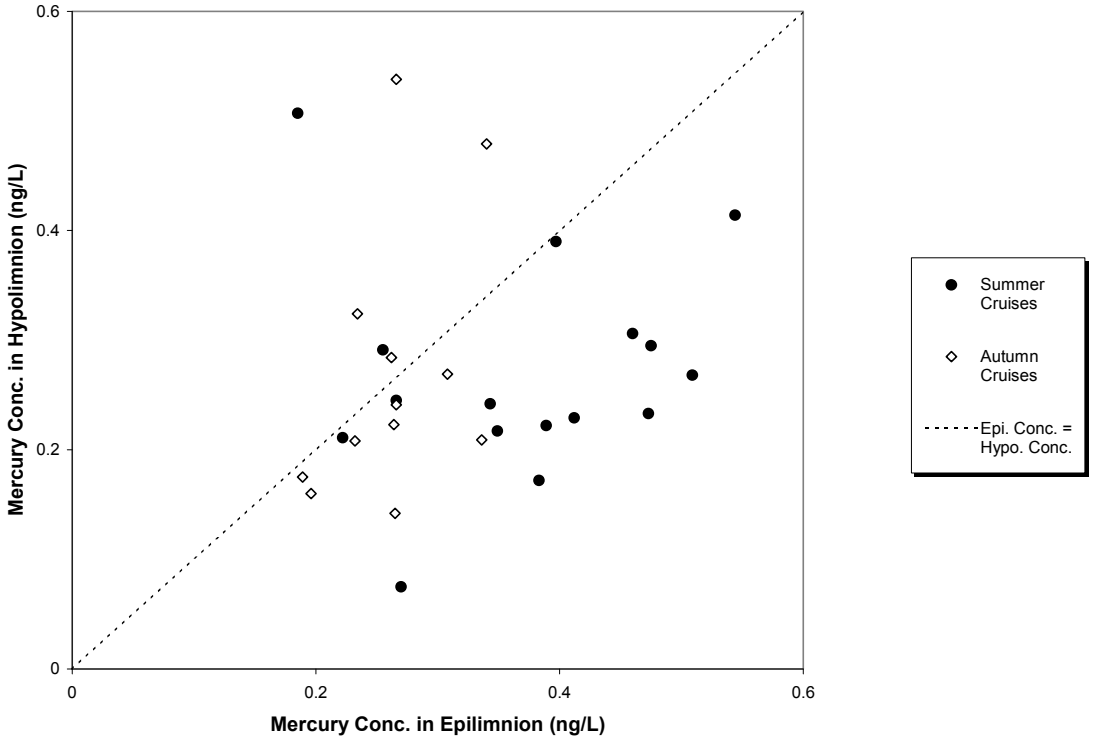
Open-lake samples were collected at depths ranging from 1 to 150 m. The correlation between sampling depth and mercury concentration (both log-transformed) was weak for particulate (r^2 = 0.057) mercury, and did not differ significantly from 0 (p = 0.539). The correlation between depth and concentration for total mercury (r^2 = -0.203) was also somewhat weak, but differed significantly from 0 (p = 0.0235). The overall weak correlation between depth and concentration may be due to station variability and variability among cruises conducted during completely mixed or thermally stratified conditions. If correlations are calculated based on only the samples collected during stratified conditions, (i.e., cruises during late summer and autumn months), the negative correlation for total mercury strengthens (r^2 = -0.393, p = 0.0002), while the particulate mercury correlation remains weak (r^2 = 0.047, p = 0.666). The correlation is presented graphically in Figure 5-3. While the relationship does not appear strong, concentrations collected at depths above (shallower than) 40 meters were significantly greater than those collected below 40 meters, based on a two-sample *t*-test (p = 0.0008).

Figure 5-3. Total Mercury Concentration versus Sample Depth During Stratified Conditions



To further account for station and cruise variability, a paired *t*-test was used to compare the mercury concentration at the deeper depth (hypolimnion) to the concentration at the shallower depth (epilimnion) where samples were collected at two depths for a given cruise and station. Two sample pairs for which both depths were either above 20 meters or below 20 meters were not included in the analyses, leaving 27 pairs for particulate mercury and 28 pairs for total mercury. These pairs were collected either during a late summer cruise (August 1994, August 1995) or an autumn cruise (October/November 1994, September/October 1995). When tests were conducted separately by these seasonal categories, there was a significant difference between the two depths for total mercury during the late summer (p = 0.0141), where the concentration was greater in the hypolimnion, but not for the autumn (p = 0.7337). These comparisons are shown in Figure 5-4. There were no significant differences between the two depths for either season for particulate mercury (Summer: p = 0.1230, Autumn: p = 0.7867). The lack of a difference between depths during the autumn cruises may be due to a decomposing thermocline late in the fall season (i.e., the end of stratification).

Figure 5-4. Total Mercury Concentrations at Stations with Samples from Multiple Depths



Statistical comparisons were also conducted to compare mercury concentrations for the two seasonal categories defined above separately for the epilimnion and hypolimnion samples. Based on two-sample *t*-tests with the Satterthwaite correction for differences in variability, there was a significant difference in total mercury concentration between the two seasons for the shallower, epilimnion samples (Summer > Autumn, $p<0.004$), but not for the deeper, hypolimnion samples ($p = 0.766$). Therefore, it would appear that the cruise differences discussed in the previous section, (i.e., the low concentrations in the autumn 1995 cruise) were mainly driven by concentration differences in the epilimnion rather than in the hypolimnion. For particulate mercury there was a significant difference for both the epilimnion (Summer>Autumn, $p = 0.010$) and hypolimnion (Summer>Autumn, $p = 0.002$) samples. Therefore, it would appear that the cruise differences in particulate mercury were driven by differences in both stratification levels of the lake.

5.1.4 Mercury Forms

Total and particulate phases of mercury were measured in Lake Michigan during the LMMB Study, and mercury in the dissolved phase was calculated by subtraction. Calculated dissolved mercury concentrations ranged from -0.12 ng/L to 0.75 ng/L. The calculated dissolved mercury concentrations for six samples were negative, including three samples collected at the station in Lake Huron, and three others from different stations collected during the August 1994 cruise. These negative values generally reflect the low concentrations of total mercury in the samples overall, and reflect the analytical uncertainties in both the total and particulate mercury concentrations for the samples. Dissolved mercury concentrations differed significantly by cruise ($p = 0.0077$), but not by station ($p = 0.1730$), based on ANOVA models (results log-transformed when possible prior to analysis). Tukey pairwise comparisons between cruises revealed that the dissolved mercury concentration during March/April 1995 was significantly greater than the concentration during August 1994. Descriptive statistics of calculated dissolved mercury concentrations are presented in Table 5-4 below. The relative standard deviations

(RSDs) for dissolved mercury during each cruise are greater than the RSDs for particulate or total mercury. This is because the dissolved mercury results were calculated, rather than measured, which increases the variability of the results.

Table 5-4. Mean Dissolved Mercury Concentrations by Cruise

Sampling Cruise	N	Mean (ng/L)	Median (ng/L)	Range (ng/L)	SD (ng/L)	RSD (%)
June 1994	12	0.19	0.16	0.078 to 0.42	0.097	50
August 1994	23	0.13	0.11	-0.12 to 0.36	0.13	100
Oct./Nov. 1994	18	0.21	0.18	0.055 to 0.51	0.14	66
March/April 1995	23	0.28	0.27	-0.076 to 0.75	0.17	62
August 1995	23	0.24	0.24	-0.026 to 0.43	0.13	52
Sept./Oct. 1995	21	0.19	0.19	0.033 to 0.31	0.070	37

In addition, the ratio of particulate to total mercury was calculated for each sample. For five of the six cruises, the mean ratios were below 0.50 (i.e., total mercury concentration more than double the particulate mercury concentration), ranging from 0.24 to 0.46. The only cruise for which this was not true was the August 1994 cruise, which had a mean ratio of 0.68. These differences between the August 1994 cruise and the rest of the data do not appear to be due to seasonality, as seen by the much lower ratios for the August 1995 cruise (mean=0.36).

5.1.5 Other Factors Affecting Tributary Mercury Concentrations

In previous studies, it has been observed that mercury concentration is correlated positively with DOC and negatively with pH (Watras *et al.*, 1995). Samples were analyzed for both DOC and pH during the LMMB Study. However, the samples collected for DOC and pH were not the same samples in which mercury was analyzed. While pH and DOC samples were collected at the same stations during the same day that mercury samples were collected, the sample depths were generally not the same. Therefore, correlations between mercury and DOC and pH could not be calculated. However, if mercury was associated with either pH or DOC, then any spatial or temporal differences observed in mercury may also be observed in the other parameters, either in the same direction (DOC) or opposite direction (pH).

To assess this possible relationship, ANOVA models for the effect of station and cruise were conducted for both pH and DOC. While pH and DOC samples were collected at more stations and cruises than those for which mercury samples were collected, these added samples were not included in the analyses. Based on the ANOVA models, pH did not differ significantly among the 15 Lake Michigan stations for which mercury samples were collected ($p=0.941$), but DOC concentrations did differ significantly among stations ($p=0.0017$; results were log-transformed prior to analysis). Subsequent Tukey pairwise comparisons showed that the DOC levels at Station 72M were significantly lower than for three other stations (180, 280 and 340). However, this was not consistent with the mercury results, as the mean mercury concentration for this station was slightly greater than the overall mean for both the particulate and total fractions. ANOVA comparisons of pH and DOC among cruises showed that mean pH differed significantly among cruises ($p<0.0001$), but mean DOC did not differ significantly ($p = 0.0531$; results were log-transformed prior to analysis). Subsequent Tukey pairwise comparisons showed that pH during the two August cruises was significantly greater than during the spring 1995 and two autumn cruises, and that mean pH during the June 1994 cruise was significantly greater than during the autumn 1994 and spring 1995 cruises. This shows some evidence of an inverse relationship, as total mercury peaked in the spring, while pH was lowest.

5.2 Quality Implementation and Assessment

As described in Section 1.5.5, the LMMB QA program prescribed minimum standards to which all organizations collecting data were required to adhere. The quality activities implemented for the mercury monitoring portion of the study are further described in Section 2.6 and included use of SOPs, training of laboratory and field personnel, and establishment of MQOs for study data. A detailed description of the LMMB quality assurance program is provided in *The Lake Michigan Mass Balance Study Quality Assurance Report* (USEPA, 2001b). A brief summary of the quality of the open-lake mercury data is provided below.

Quality Assurance Project Plans (QAPPs) were developed by the PIs and were reviewed and approved by GLNPO. Each researcher trained field personnel in sample collection SOPs prior to the start of the field season and analytical personnel in analytical SOPs prior to sample analysis. Each researcher submitted test electronic data files containing field and analytical data according to the LMMB data reporting standard prior to study data submittal. GLNPO reviewed these test data sets for compliance with the data reporting standard and provided technical assistance to the researchers. In addition, each researcher's laboratory was audited during an on-site visit at least once during the time LMMB samples were being analyzed. The auditors reported positive assessments and did not identify issues that adversely affected the quality of the data.

As discussed in Section 2.6, data verification was performed by comparing all field and QC sample results produced by each PI with their MQOs and with overall LMMB Study objectives. Analytical results were flagged when pertinent QC sample results did not meet acceptance criteria as defined by the MQOs. These flags were not intended to suggest that data were not useable; rather they were intended to caution the user about an aspect of the data that did not meet the predefined criteria. Table 5-5 provides a summary of flags applied to the open-lake mercury data. The summary includes the flags that directly relate to evaluation of the MQOs to illustrate some aspects of data quality, but does not include all flags applied to the data to document sampling and analytical information, as discussed in Section 2.6. One particulate mercury result was qualified as invalid due to a suspected leak in the sample, and was not used in the analyses of open-lake mercury concentrations presented in this report.

Table 5-5. Summary of Routine Field Sample Flags Applied to Mercury in Open-lake Samples

Flag	Number of QC samples		Percentage of Samples Flagged (%)	
	Particulate	Total	Particulate	Total
INV, Invalid Result	—	—	0.8% (1)	0
DDL, Below Daily Detection Limit	—	—	8% (10)	4% (5)
EHT, Exceeded Holding Time	—	—	0	0
FDL, Failed Lab Duplicate	45 lab duplicate groups	63 lab duplicate groups	8% (10)	18% (22)
FFD, Failed Field Duplicate	18	18	7% (8)	6% (7)
FFR, Failed Field Blank	13	17	0	0
FPC, Failed Lab Performance Check	114		19% (23)	26% (33)

The number of routine field samples flagged is provided in parentheses. The summary provides only a subset of applied flags and does not represent the full suite of flags applied to the data.

Holding time flags were applied based on a criterion of 120 days between sampling and analysis. All data met this criterion, with a maximum lag between sampling and analysis of 115 days.

The analytical sensitivity of field samples was assessed through analysis of daily detection limits. A different limit was calculated for each day of analysis, with a maximum of 12 field samples associated with a given daily detection limit. A "below daily detection limit" flag (DDL) was applied if a given field sample concentration fell below its associated daily detection limit. The DDL flag was applied to 8% of particulate mercury sample results and to 4% of total mercury sample results.

Field reagent blanks were analyzed to assess the potential for contamination of routine field samples. A total of 24 valid field reagent blanks were analyzed, with concentrations ranging from -0.33 ng/L to 0.099 ng/L. In accordance with the researcher's data qualifying rules for field blanks, these blank results were compared to a maximum of 0.10 ng/L. Because this level was never exceeded, no blanks or associated samples were flagged with associated blank failure.

A total of 31 field duplicate samples and 133 laboratory duplicate samples were analyzed to assess precision. The laboratory duplicate samples include both replicate analyses of field samples and field duplicates, with up to 3 duplicates associated with a given field sample. From each cruise (except the January 1995 cruise that visited only two sites), duplicate samples were collected at one to three stations. In accordance with the researcher's data qualifying rules for field and laboratory duplicates, samples were flagged for a failed duplicate (FFD or FDL) if the relative percent difference (RPD) (or relative standard deviation, RSD, where more than one laboratory duplicate was prepared for a given field sample) between results for a sample and its duplicate was greater than 20%. This criterion was not met for 15 field duplicate pairs and for 32 laboratory duplicate groups. The maximum field duplicate RPD was 96%, and the maximum laboratory duplicate RPD/RSD was 109%. While these RPDs were high, they were based on low concentrations which were either below the daily detection limit or only slightly above.

Laboratory performance check samples were used to monitor analytical bias. In accordance with the researcher's data qualifying rules for laboratory performance checks, samples were flagged for a failed performance check (FPC) if the associated concentration was outside the concentration range of 0.80 to 1.2 ng (corresponding to 80% to 120% recovery). Based on application of this criterion, 23% of the field samples were associated with a failed performance check. These flags were applied based on 28 performance check results exceeding 1.2 ng, with a maximum of 1.7 ng. Based on an analysis of laboratory spikes, blank contamination, and other internal QC data, the QC coordinator did not qualify any samples as high or low biased.

As discussed in Section 1.5.5, MQOs were defined in terms of six attributes: sensitivity, precision, accuracy, representativeness, completeness, and comparability. GLNPO derived data quality assessments based on a subset of these attributes. For example, system precision was estimated as the mean RPD between the results for field duplicate pairs. Similarly, analytical precision was estimated as the mean RPD or RSD between the results for laboratory duplicate groups. Table 5-6 provides a summary of data quality assessments for several of these attributes for open-lake data. The mean RPD for field duplicate sample results was 28% for particulate mercury and 21% for total mercury, where both the sample and duplicate results were greater than the daily detection limit. The mean RPD/RSDs for laboratory duplicate samples were 15% and 17% for particulate and total mercury, respectively, where all results were above the daily detection limit.

Analytical bias was evaluated by calculating the mean recovery of laboratory performance check samples (LPC). Results indicated a slight positive bias, with a mean recovery of 110%. This bias applies to both particulate and total mercury, as the LPC samples were not associated with a specific fraction.

Analytical sensitivity was evaluated by calculating the percentage of samples reported below the daily detection limit. The mean daily detection limit was 0.063 ng/L, and ranged from 0.010 ng/L to 0.26 ng/L. The majority of field samples were above the corresponding daily detection limit, with only 8% of

particulate mercury sample results and 4% of total mercury sample results falling below the given limit. Results from these samples were not censored and were used as reported in the analysis of open-lake mercury data presented in this report.

Table 5-6. Data Quality Assessment for Mercury in Open-lake Samples

Parameter	Assessment	
	Particulate	Total
Number of Routine Samples Analyzed	121	125
Number of Field Duplicates Analyzed	18	18
System Precision, Mean Field Duplicate RPD (%), <DDL[a]	—	39% (1)
System Precision, Mean Field Duplicate RPD (%), >DDL[a]	28% (16)	21% (13)
Analytical Precision, Mean Lab Duplicate RPD (%), <DDL[a]	11% (1)[b]	60% (3)[b]
Analytical Precision, Mean Lab Duplicate RPD (%), >DDL[a]	15% (47)[b]	17% (68)[b]
Analytical Bias, Mean LPC (percent recovery)	110% (111)	
Analytical Sensitivity, Samples reported as <DDL (%)	8%	4%

[a] Number of Sample/duplicate pairs used in the assessment is provided in parentheses
[b] Includes lab duplicate pairs of field duplicates
DDL = Daily Detection Limit
LPC = Laboratory Performance Check

As previously shown in Table 5-3, all the particulate mercury results that were below the DDL were collected in the August 1994 cruise. However, the mean concentration from that cruise was significantly greater than many of the other cruises. The high number of below DDL results from that cruise is due to a DDL exceeding 0.23 ng/L, run on a day for which samples from this cruise only were analyzed. This was the only DDL exceeding 0.20 ng/L run on days for which particulate samples were analyzed. This high DDL, in addition to the greater particulate mercury concentrations in this cruise, suggests the possibility of slight contamination occurring during the analysis of these samples. In general, the variability of the DDLs was approximately equal to that of the particulate mercury results. The standard deviation of the DDLs was 0.067 ng/L, while the standard deviation of the particulate mercury results was 0.058 ng/L. This is more likely due to the relatively low level of particulate mercury concentrations in Lake Michigan than to any QC issues with the laboratory. However, it is possible that some of the temporal differences observed in the particulate mercury may be partially due to some analytical differences between the analytical batches associated with the different cruises.

5.3 Data Interpretation

5.3.1 Mercury Levels in Lake Michigan

The mean and median total mercury concentrations from the 15 stations located in Lake Michigan were 0.33 ng/L and 0.30 ng/L, respectively. Comparisons of this mean and median to previous studies are complicated by changes in analytical methods and the increased use of clean sampling techniques in recent years. Therefore, there are no historical Lake Michigan data against which to compare the current results.

The mean concentrations from the LMMB Study were below those measured in other lakes using clean sampling techniques and comparable analytical methodology. For example, Watras, *et al.* (1995) measured total mercury and calculated particulate mercury for 23 lakes in Wisconsin in 1993. The mean

total mercury concentration from these lakes was 1.48 ng/L for total mercury and 0.37 ng/L for particulate mercury. Watras and Bloom (1992) also measured total mercury in the lower trophic levels of an acidified basin and a reference basin in Little Rock Lake in Wisconsin in 1990. The mean total mercury concentration in the reference basin was 0.0011 ng/g, or 1.1 ng/L. Mercury concentrations similar to those measured in Lake Michigan were measured in three drainage lakes in Manitoba, with total mercury concentrations ranging from 0.2 to 1.1 ng/L (Bloom and Effler, 1990, based on their personal communication with J.W.M. Rudd).

The differences in mercury concentration between Lake Michigan and the lakes measured in previous studies are not surprising, given the inherent differences between the lakes. In addition to the greater area and depth of Lake Michigan, there are also differences in the chemistry of the lakes. For example, the mean DOC and pH for the LMMB Study were 1.57 mg/L and 8.20, respectively. In contrast, mean DOC concentrations and pH measured in 23 Wisconsin lakes were 6.62 mg/L and 6.17, respectively (Watras *et al.*, 1995). Monson and Brezonik (1998) also reported DOC concentrations in 12 lakes in northeastern Minnesota that were similar to those in the Wisconsin lakes, ranging from 4.5 to 10.2 mg/L, and similar pH levels, ranging from 6.2 to 6.8. In addition, correlations between total mercury and various chemical parameters were reported by Watras *et al.* (1995), with mercury having a strong positive correlation with DOC ($r^2 = 0.93$) and a strong negative correlation with pH ($r^2 = -0.51$). However, these correlations do not necessarily explain the mercury differences between Lake Michigan and the other two studies, as correlations do not necessarily imply a causal relationship.

5.3.2 Comparison to Regulatory Limits

The freshwater water quality criterion established by EPA for human health protection is 50 ng/L for mercury. This is more than an order of magnitude above the mean concentration measured in the lakes in this study (0.33 ng/L). The mean concentration in this study is also less than the criteria for human health (1.8 ng/L) and wildlife (1.3 ng/L) for the Great Lakes states.

5.3.3 Lateral Variation

Neither total mercury nor particulate mercury differed significantly between the 15 stations in Lake Michigan at which samples were collected. This lends support to the theory that the primary source of mercury to Lake Michigan is atmospheric (Sullivan and Mason, 1998), rather than riverine. A larger level of riverine input would have been suggested if stations located closer to tributaries, especially GB24M, had higher levels of mercury. The lack of spatial variability in concentrations in Lake Michigan was also supported by the generally homogeneous levels of pH and DOC in Lake Michigan samples. Only DOC exhibited significant differences between stations, as one northern Lake Michigan station had a lower DOC concentration than three of the other stations.

5.3.4 Temporal Variation

Seasonal patterns in the total and particulate results were not clear, due to differences in the timing of the cruises in the two years of the study. For total mercury, the mean concentration was greatest during the fourth cruise (March/April 1995), and was significantly greater than for two other cruises. This cruise was the only one that occurred during the spring, which suggests that the difference may be due to a seasonal effect. Peak mercury concentrations in lakes during the spring were also observed by Monson and Brezonik (1998) in 12 lakes in Minnesota and by Bloom and Effler (1990) in the Onondaga Lake in New York. However, seasonal patterns during summer and autumn seemed to differ between the two years in the LMMB Study. The September/October 1995 cruise had the lowest mean total mercury concentration and was significantly lower than the other two cruises run in 1995. The October/November 1994 cruise did not exhibit a similar drop in concentration, but in fact, had a mean mercury concentration

slightly greater than the other two 1994 cruises. These differences in patterns may have been partially due to a calcite precipitation event occurring in 1995 (Sullivan and Mason, 1998). A drop in mercury concentration has not generally been observed in prior studies. Monson and Brezonik (1998), in fact, observed an increase in concentration in autumn compared to summer. The lower concentration in autumn 1995 is also unexpected, based on the lower productivity level in 1994 (Sullivan and Mason, 1998).

Unlike total mercury, particulate mercury concentrations did not peak during the spring, instead they were greatest in the June 1994 and August 1994 cruises. Similar to total mercury, the lowest concentrations were observed during the September/October cruise. These results were not consistent with the productivity level differences in the two years. It is worth noting that the August 1994 cruise had greater daily detection limit values than the other cruises. Based on the low levels and variability of concentrations measured in this study, any differences could have been strongly affected by slight levels of contamination.

Seasonal differences were also affected by lake stratification. The four late summer and autumn cruises included samples from multiple depths at most stations, representing the epilimnion and hypolimnion levels of the lake. For total mercury, the concentrations in the epilimnion were significantly greater in the summer compared to the autumn.

While mercury concentrations differed by cruise, DOC concentrations did not. This was unexpected, given the strong positive correlations observed between DOC and total mercury in past studies. Mean pH did differ significantly between cruises, with peak levels occurring during summer, and lower levels occurring during the spring and autumn.

5.3.5 Vertical Variation

Total and particulate mercury concentrations were generally higher at depths closer to the surface, though the effect of depth on concentration was not strong. Higher concentrations were expected near the surface, because atmospheric deposition is considered to be the primary source of mercury input (Sullivan and Mason, 1998). This effect of depth was greater during the late summer cruises, i.e., during peak stratification conditions. The timing of the two autumn cruises differed, as the autumn 1994 cruise began in mid-October, whereas the autumn 1995 cruise began in mid-September. However, there were not enough pairs collected during these two cruises to assess the effect the timing difference had on stratification of mercury.

Samples analyzed for total mercury were also collected at different depths and seasons from Lake Onondaga in New York (Bloom and Effler, 1990). Similar to the current study, differences in concentration between surface and hypolimnion depths (measured at 18 m) were greatest during the summer. However, the direction of the difference was not the same, as the total mercury concentration was greater in the hypolimnion. Similar to the current study, the difference between depths was minimal in autumn. Total mercury concentrations in the hypolimnion also exceeded concentrations in the epilimnion in Devil's Lake in Wisconsin (Herrin, *et al.*, 1998). While epilimnion concentrations were similar to those observed in this study (ranging from 0.10 to 1.0 ng/L), hypolimnion concentrations were as high as 2.0 ng/L.

A possible difference between the relationship between depth and concentration in Lake Michigan and in the other lakes is the greater depth of Lake Michigan. The maximum depths of Lake Onondaga and Devil's Lake are 20.5 m and 14 m, respectively. The depths of the Lake Michigan stations from which mercury samples were collected ranged from 27 m to 259 m. This difference could have played a role in the relationship between depth and mercury concentration. For smaller, shallower lakes, the role of

sediment resuspension, compared to atmospheric input, will likely be greater than for larger, deeper lakes. This increased role of sediment resuspension would result in a greater level of mercury in the hypolimnion compared to the surface of the lake.

5.3.6 Mercury Fractions and Forms

For five of the six cruises, the majority of the total mercury was in the dissolved, rather than particulate, phase. This result is similar to that observed by Watras *et al.* (1995) in 23 Wisconsin lakes. However, Bloom and Effler (1990) found that the majority of total mercury was in the particulate fraction in Lake Onondaga. In addition, Bloom and Effler observed that the percentage of total mercury in the particulate fraction was greatest in the autumn. The authors hypothesized that this was due to the coagulation of suspended matter after lake turnover.